Studies on Aromatic Amine-Epoxy Novolac Systems

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ABSTRACT

Cure kinetics of an aromatic amine (DDM) cured epoxy novolac systems were studied. Parameters such as heat of reaction, rate constants and activation energy were evaluated using DSC studies. Further, mechanical properties of the cured laminate have been reported.

INTRODUCTION

Epoxy resins are widely used in diverse applications such as surface coatings, printed circuit boards, plotting of electronic components, rigid foams, adhesives and fibre reinforced composites. An understanding of the chemical reactions in the curing process of the epoxy resins with various hardeners is as important as the characterisation of the product after curing. The kinetics of the curing reaction of Diamino Diphenyl Methane (DDM) with epoxy resins like Diglycidyl Ether of Bisphenol A (DGEBA) and Triglycidyl ether of p-amino phenol (TrGPAP) were studied thoroughly and well documented[1-4]. Prepregging processes and hybridisation processes with different epoxy resins to tailor-make the necessary properties needed for a particular application necessitate the knowledge of cure kinetics of those resins with the curing agents (hardeners) used either alone or in combination. Cure kinetics of epoxy-novolac resin which is widely used in high temperature applications have not been studied with DDM as the curing agent and kinetic parameters estimated.

In the present work, the DSC technique is employed to study the cure kinetics of the epoxy novolac/DDM resin system. The overall kinetic parameters of the curing reactions such as the heat of reaction, the rate constant, activation energy, and frequency factor were estimated based on dynamic and isothermal DSC scans. The mechanical properties of the glass-epoxy novolac/DDM laminate are also reported.

EXPERIMENTAL

Materials

Epoxy Novolac (EPN 1138) was obtained from Hindusthan Ciba Geigy, India. The resin was kept in a vacuum oven at 353 K and 10 mm of Hg for 1 hour to remove moisture and entrapped vapour. DDM was purified by recrystallisation, dried and kept in vacuum at 333 K for 2 hours. Epoxy equivalent of the resin was 177 WPE, as estimated by hydrohalogenation method. Viscosity at 333 K was found to be 490 P, using Brookfield viscometer.

Epoxy Novolac resin and DDM were heated to 353 K separately and mixed in the stoichiometric proportion. The mixture was immediately transferred to ice-bath to arrest the reaction. 10-15 mg of the sample was placed in aluminium DSC pan and were run on a Perkin-Elmer DSC-2. Isothermal scans were done at 373 K, 393 K and 403 K and dynamic scans were carried out at the heating rates of 2.5 K/min, 5 K/min and 10 K/min.

DATA ANALYSIS, RESULTS AND DISCUSSION

The relationship between an isothermal DSC signal and the rate and extent of cure has been reviewed by Prime[5]. A general rate law that has proven useful for studying the epoxy cure reaction is[4,5]

$$\frac{d\alpha}{dt} = (k_1\alpha + k_1') (1 - \alpha) (B - \alpha) \quad (1)$$

where $d\alpha/dt$ is rate of conversion, α is degree of conversion, k_1, k_1' are rate constants and B is a stoichiometric ratio. The curing reaction of epoxy resin may follow the nth order or autocatalytic kinetics. Curing reaction obeying equation (1) operates between two extremes. At the one extreme, when the concentration of the impurity is zero, the cure would be autocatalysed, exhibiting an induction time. The maximum rate occurs at 30-40% conversion. At the other extreme, where $k_1' \gg k_1$, curing would behave according to the nth order kinetics, with the maximum rate at $t = 0$.

The isothermal scans shown in Figure 1,

exhibiting an induction time and the plot of α vs t (Figure 2) for isothermal scans, showing the maximum rate at 30-40%, obtained in the present studies shows that the reaction of the epoxy-novolac/DDM system exhibits autocatalytic behaviour.

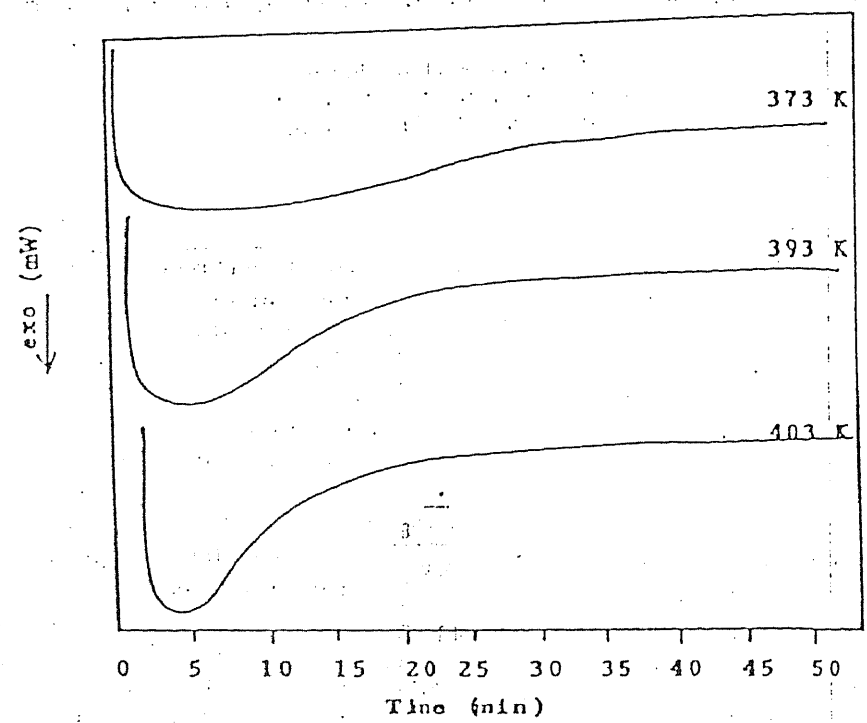

Figure 1 Isothermal DSC thermograms of epoxy novolac-DDM at 370 K, 393 K and 403 K

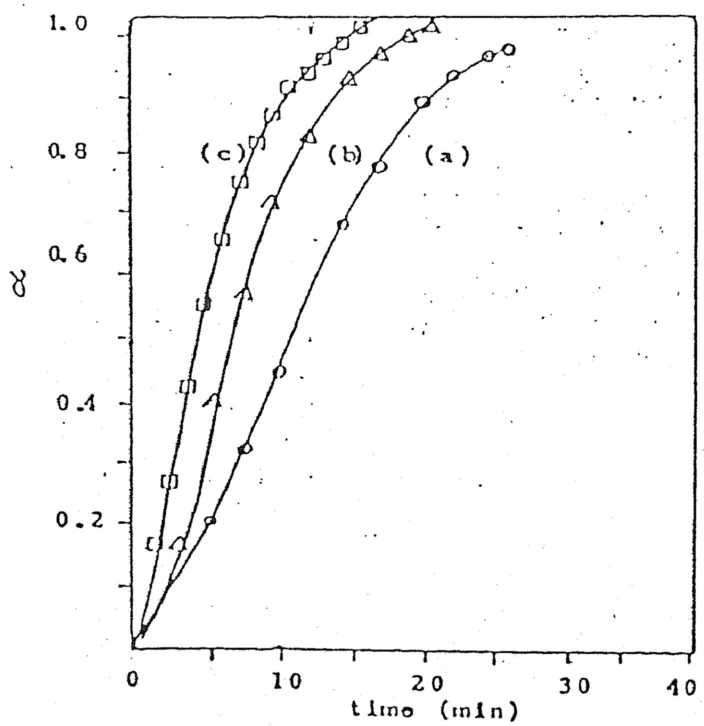

Figure 2 Plot of degree of cure with time at: 373 K (a), 393 K (b) and 403 K (c)

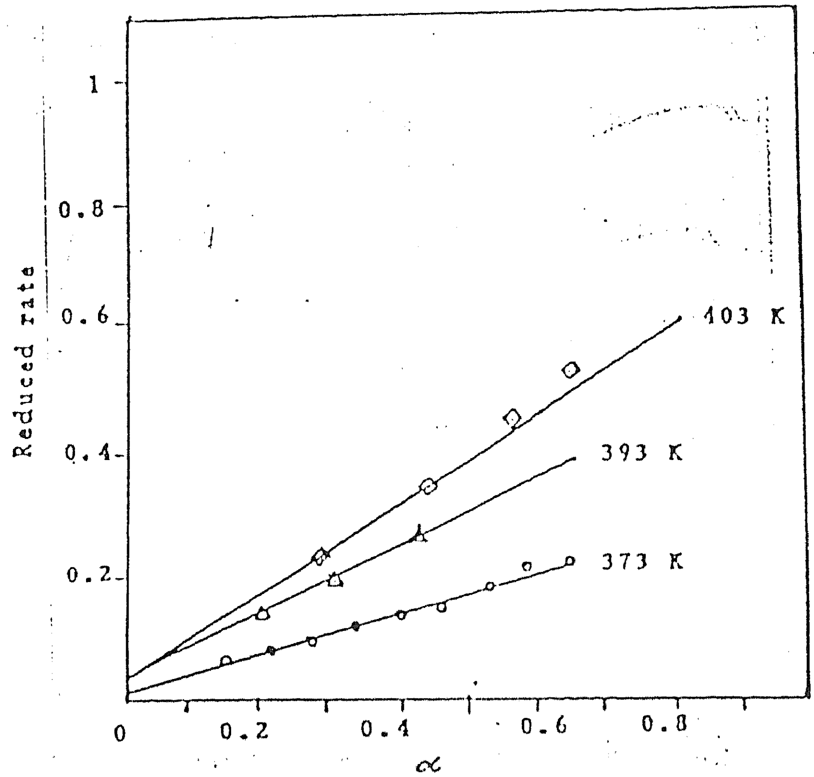

Figure 3 Plot of reduced rate vs degree of conversion

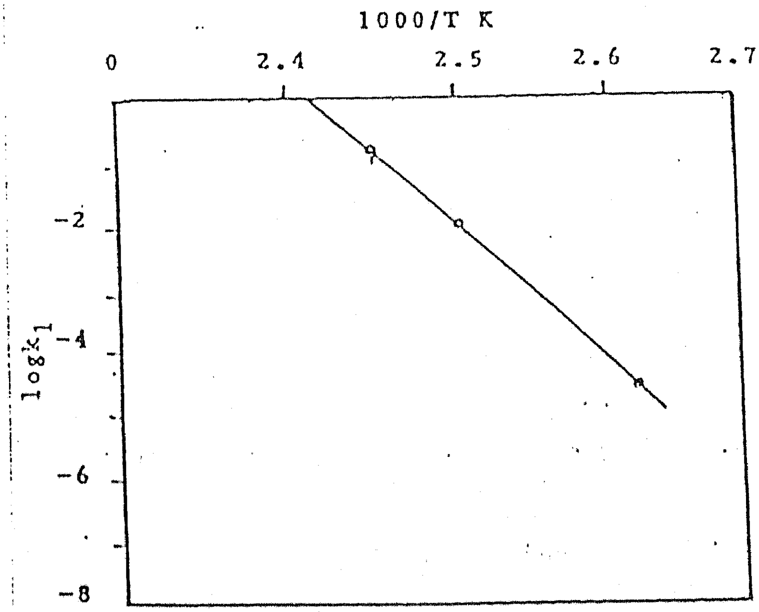

Figure 4 Plot of logarithm or rate constant reciprocal absolute temperature

The rate constants, k_1, k_1' were calculated from the slope and the intercepts of the plot of reduced rate vs. degree of conversion (Figure 3). The activation energy and frequency factor were calculated from the Arrhenius equation

$$k_1 = A \exp - E / RT \quad (2)$$

The plot log k_1 vs $1/T$ (Figure 4) revealed that the simple Arrhenius Kinetics were followed upto at least 70-75% of completion.

Figure 5 shows the dynamic scans at the heating rates of 2.5 K/min, 5 K/min and 10 K/min. The exotherms were analysed to obtain two basic

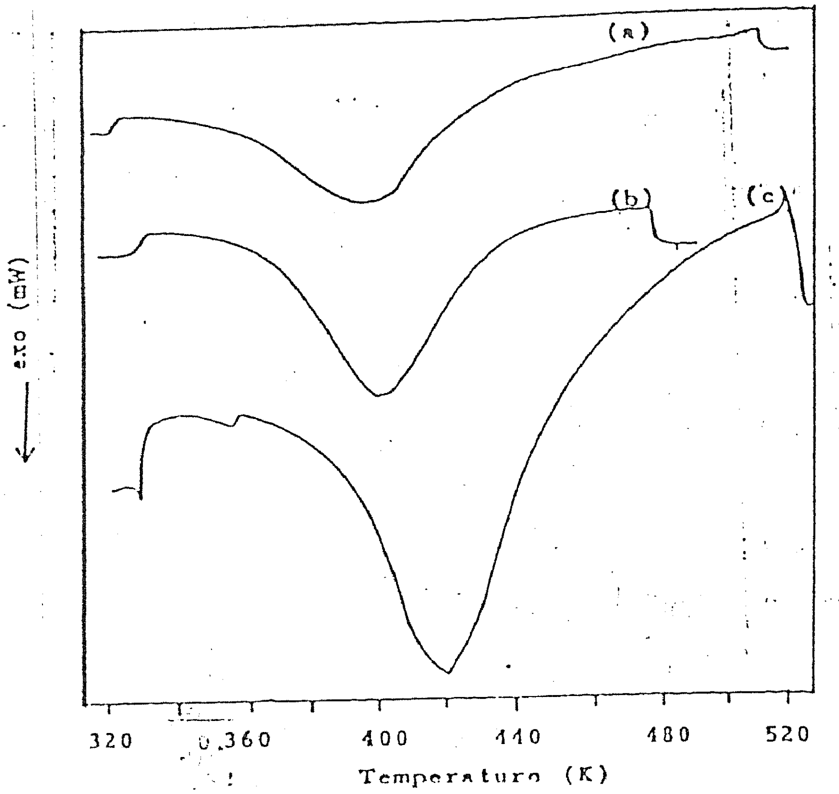

Figure 5 Dynamic DSC thermograms of epoxy novolac-DDM at heating rates; 2.5 K/min (a), 5 K/min (b) and 10 K/min (c)

Table 1 Curing characteristics of epoxy/novolac/DDM at different scan rates

Heating Rate (K/min)	T_i(K)	T_p(K)	T_f(K)	Curing Range (K)	T_g(K)	ΔH(Cal/g)	E (KCal/mole)
2.5	330	402	525	195	545	62.1	11.67+
5.0	335	404	485	150	552	57.0	12.70*
10.0	360	420	535	175	556	51.0	

+ Bascom & Pyre method   * Barton method

parameters, the peak height, dH/dt, and the area under the exotherm, as well as some characteristic temperatures such as the temperature of onset of curing (T_i), the peak maximum temperature (T_p), the temperature of the completion of curing (T_f) and glass transition temperature (T_g). Table 1 shows all such data obtained.

The peak temperatures at different heating rates were used to calculate E from

$$E = \frac{\log \phi}{0.4567 \ (1/Tp)} \qquad (3)$$

based on the work of Bascom and Pyre[6] and Ozawa[7]. E was obtained from the slope of the plot

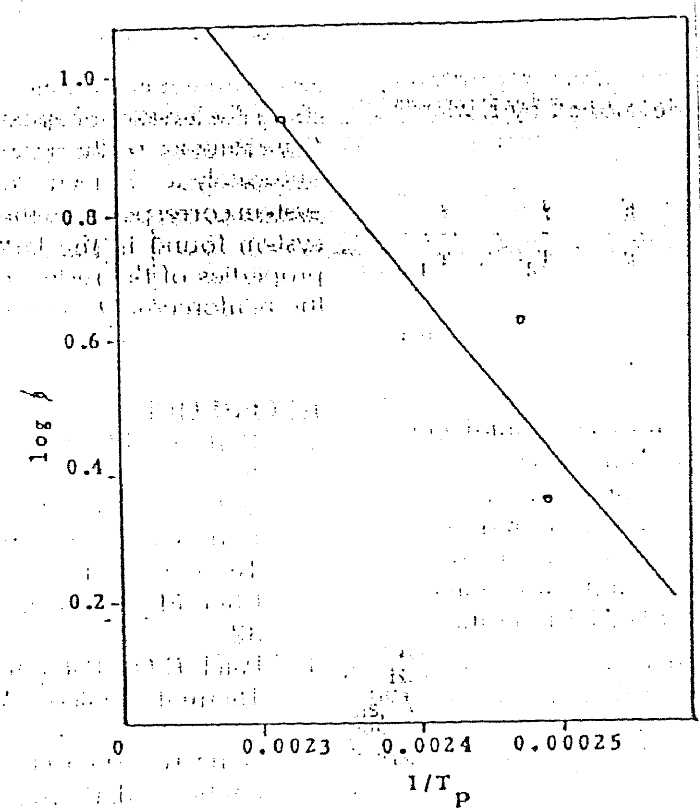

Figure 6 Plot of logarithm of heating rate vs. inverse peak temperature

Table 2 Kinetic data obtained from isothermal scans

Temperature (K)	ΔHrxn (Cal/g)	k_1(1/min)	k_1^1(1/min)	A(1/min) x 10^{-5}	E (KCal/mole)
373	61.20	0.35	0.015	1.80	
393	60.25	0.65	0.020	1.70	11.83
403	65.00	0.78	0.040	1.61	

Table 3 Comparison of E values of different epoxy resins with DDM

Epoxy Novolac	DGEBA [8]	TrGPAP [3]
12.06 KCal/mole	12.06 KCal/mole	13.6 KCal/mole

of $1/T$ vs. $\log \phi$ (Figure 6).

E was also calculated from a method based on two dynamic DSC scans developed by Barton[2] using the equation:

$$\ln \frac{(d\alpha/dt)_{T_1}}{(d\alpha/dt)_{T_2}} = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

where Ts are temperatures for a constant degree of conversion at different heating rates.

The activation energy calculated from three different methods (equations 2, 3 and 4) is tabulated in Table 2. The values obtained are found to be almost the same and correspond to the values obtained for DGEBA/DDM (Table 3).

The tensile, flexural, interlaminar shear strength and Izod impact tests were carried out as per the ASTM standards, and the values are shown in Table 4.

Table 4 Mechanical properties of glass-epoxy novolac/DDM system

Property	Epoxy Novolac/DDM
Fibre Content, w/w	72.00%
Tensile Strength, MPa	311.80
Tensile Modulus, GPa	19.85
Flexural Strength, MPa	447.00
ILSS, MPa	32.20
Impact Strength, Kgf/cm	149.40

CONCLUSIONS

Isothermal and dynamic scans have been used to study the kinetics of epoxy novalac/DDM system. Cure kinetics of the system were found to follow autocatalytic. E value of epoxy novalac/DDM system corresponds to the value of DGEBA/DDM system found in the literature. The mechanical properties of the resin system with glass cloth as the reinforcement were found and reported.

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